IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s):

SHIMOKAWA, et al.

Filed:

October 9, 2001

For:

PB-FREE SOLDER-CONNECTED STRUCTURE AND

ELECTRONIC DEVICE

CLAIM FOR PRIORITY

Assistant Commissioner for Patents Washington, D.C. 20231

October 9, 2001

Sir:

Pursuant to 35 USC 119 and 37 CFR 1.55, Applicants respectfully claim priority based on Japanese Priority Application No. 09-346,811, filed in Japan on December 16, 1997. As indicated in the Notification of Acceptance of application under 35 USC 371 and 37 CFR 1.494 or 1.495, mailed June 30, 2000, in prior application Serial No. 09/581,631, the Priority Document was received in prior application Serial No. 09/581,631.

Respectfully submitted,

ANTONELLI, TERRY), STOUT & KRAUS, LLP

William I. Solomon

Registration No. 28,565

WIS/slk

Tel.: 703-312-6600

#6

DECLARATION

I, Yoshio Miyata, 15-2, Higashi-tateishi 4-chome, Katsushika-ku, Tokyo, Japan do solemnly and sincerely declare that I well understand the Japanese language and English language and the attached English version is full, true and faithful translation of the certified copy of Japanese Patent Application No. 346811 of 1997.

And I made this solemn declaration conscientiously believing the same to be true.

This 4th day of October, 2001

Yoshio Miyata

[Name of Document]

Application for Patent

[Reference No.]

PNT970579

[Application Date]

December 16, 1997

[Destination]

Commissioner, Patent Office

[International Patent Cl.] H01L 27/00

[Title of the Invention] Lead-Free Solder-Connected Structure And Electric Device

(No. of Claims) 13

[Inventor]

[Address] 292, Yoshida-cho, Totsuka-ku, Yokohama-shi,

Kanagawa-ken

Hitachi, Ltd.

Production Engineering Research Laboratory

(Name)

Hidemu SHIMOKAWA

[Inventor]

[Address] 292, Yoshida-cho, Totsuka-ku, Yokohama-shi,

Kanagawa-ken

Hitachi, Ltd.

Production Engineering Research Laboratory

[Name]

Tasao SOGA

(Inventor)

[Address] 292, Yoshida-cho, Totsuka-ku, Yokohama-shi,

Kanagawa-ken

Hitachi, Ltd.

Production Engineering Research Laboratory

[Name] Hiroaki OKUHIRA

[Inventor]

[Address] 292, Yoshida-cho, Totsuka-ku, Yokohama-shi,

Kanagawa-ken

Hitachi, Ltd.

Production Engineering Research Laboratory

(Name) Toshiharu ISHIDA

[Inventor]

[Address] 292, Yoshida-cho, Totsuka-ku, Yokohama-shi,

Kanagawa-ken Hitachi, Ltd.

Production Engineering Research Laboratory

[Name] Tetsuya NAKATSUKA

[Inventor]

[Address] 20-1, Josuihoncho 5-chome, Kodaira-shi, Tokyo

Hitachi, Ltd.

Semiconductor Division

[Name] Yoshiharu INABA

[Inventor]

[Address] 20-1, Josuihoncho 5-chome, Kodaira-shi, Tokyo

Hitachi, Ltd.

Semiconductor Division

[Name] Asao NISHIMURA

[Applicant]

[Identification No.] 000005108

[Name] Hitachi, Ltd.

[Representative] Tsutomu KANAI

[Agent]

[Identification No.] 100061893

[Patent Attorney]

[Name] Akio TAKAHASHI

[TEL No.] 03-3661-0071

(Appointed Agent)

[Identification No.] 100086656

[Patent Attorney]

[Name]
[TEL No.]

Kyosuke TANAKA 03-3661-0071

(Designation of Fee)

[Ledger No. for Deposit] 011626 [Amount of Payment] 21000

[List of Submitted Document]

[Object Name] Specification 1
[Object Name] Drawings 1
[Object Name] Abstract 1
[No. of Comprehensive Power of Attorney] 9003091
[No. of Comprehensive Power of Attorney] 9403294

(Necessity of Proof) Required

[Name of Document] Specification
[Title of the Invention] Lead-Free Solder-Connected
Structure And Electronic Device
[What is Claimed is]

[Claim 1]

A lead-free solder-connected structure characterized in that an Sn-Ag-Bi based lead-free solder is connected to an electrode through an Sn-Bi based layer.

[Claim 2]

A lead-free solder-connected structure according to claim 1, characterized in that said Sn-Bi based layer contains 1 to 20 wt% Bi.

[Claim 3]

A lead-free solder-connected structure according to claim 1 or 2, characterized by comprising a copper layer between said electrode and said Sn-Bi based layer.

[Claim 4]

A lead-free solder-connected structure according to claim 1 or 2, characterized in that said electrode is made of copper material.

[Claim 5]

A lead-free solder-connected structure according to any one of claims 1 to 3, characterized in that said electrode is of a lead made of an Fe-Ni based alloy or a copper based alloy.

[Claim 6]

A lead-free solder connected structure according to any one of claims 1 to 5, characterized in that said Sn-Ag-Bi based lead-free solder contains Sn as a primary component, 5 to 25 wt% Bi, 1.5 to 3 wt% Ag and up to 1 wt% Cu.

[Claim 7]

An electronic device in which a first electrode formed on an electronic component and a second electrode formed on a circuit board are electrically connected to each other, characterized in that an Sn-Bi based layer is formed on said first electrode, and said first electrode on which the Sn-Bi based layer is formed and said second electrode are connected to each other using an Sn-Ag-Bi based lead-free solder.

[Claim 8]

An electronic device according to claim 7, characterized in that said Sn-Bi based layer contains 1 to 20 wt% Bi.

[Claim 9]

An electronic device according to claim 7 or 8, characterized by comprising a copper layer between said Sn-Bi based layer and said first electrode.

[Claim 10]

An electronic device according to claim 7 or 8, characterized in that copper material is provided on said first electrode side of said Sn-Bi based layer.

[Claim 11]

An electronic device according to any one of claims 7 to 9, characterized in that said first electrode is a lead made of an Fe-Ni based alloy or a copper based alloy. [Claim 12]

An electronic device according to any one of claims 7 to 11, characterized in that said Sn-Ag-Bi based lead-free solder contains Sn as a primary component, 5 to 25 wt% Bi, 1.5 to 3 wt% Ag and up to 1 wt% Cu.

[Claim 13]

A lead-free solder-connected structure characterized in that a lead-free solder connected to an electrode is an Sn-Ag-Bi based solder containing Sn as a primary component, 5 to 25 wt% Bi, 1.5 to 3 wt% Ag and up to 1 wt% Cu. [Detailed Description of the Invention]

[Technical Field to Which the Invention pertains]

The present invention relates to a lead (Pb)-free solder-connected structure, in which electrodes such as lead frames or the like are preferably connected to each other with the use of a lead-free solder with low toxicity, and an electronic device using the same.

[Prior Art]

[0002]

In order to produce an electric circuit board by bonding electric devices (e.g. LSIs) to a circuit board

made of an organic material, for example, conventionally, there has been used a eutectic Sn-Pb alloy solder, another Sn-Pb alloy solder which has a chemical composition and a melting point each close to that of the eutectic Sn-Pb alloy solder, and other solder alloys which are obtained by adding small amounts of bithmuth (Bi) and/or silver (Ag) to the solders recited above. These solders contain about 40 wt% Pb and have a melting point of about 183°C, which permit soldering at 220 - 240°C.

With regard to electrodes of electronic devices, such as QFP (Quad Flat Package)-LSIs, to be soldered, there have been usually used those made of 42 alloy which is an Fe-Ni alloy and on which a layer of 90 wt% Sn-10 wt% Pb (hereinafter referred to as "Sn-10Pb") layer is formed. This is because such electrodes have good wettability, good preservation and no problem of formation of whiskers.

[Problem to be Solved by the Invention]

However, the lead (Pb) in the Sn-Pb solders is a heavy metal harmful to humans and pollution of the global environment caused by dumping of lead-containing products and their bad effect on living things have presented problems. The pollution of the global environment by electrical appliances occurs when lead is dissolved, by rain or the like, from the dumped lead-containing electrical appliances exposed to the weather. The

dissolution of Pb tends to be accelerated by the recent acid rain. In order to reduce environmental pollution, therefore, it is necessary to use a lead-free soldering material with low toxicity not containing lead as a substitute for the above eutectic Sn-Pb based solder which is used in large quantity and to employ a component electrode structure not containing lead as a substitute material for the Sn-10Pb layer provided on the component electrode. An Sn-Ag-Bi based solder is a promising candidate as a lead-free soldering material in terms of low toxicity, obtainability for raw materials, production cost, wettability, mechanical properties, connection reliability and the like. Soldering is usually performed at a temperature of about 220 - 240°C so as to produce compounds between an electrode of a component or a board and a solder for connection therebetween. Due to this fact, because the bonding interfaces differs from one another depending upon different kinds of combinations of solder materials and electrode materials of components, an electrode material suitable to the respective solder is required in order to obtain a stable bonding interface. [0004]

An object of the present invention is to provide a lead-free solder connected structure in which an Sn-Ag-Bi based lead-free solder with low toxicity is used for electrodes of lead frames, etc. and which has a stable

bonding interface and an enough bonding strength.

Another object of the invention is to provide an electronic device with the use of an Sn-Ag-Bi based lead-free solder with low toxicity, which has a stable bonding interface with respect to a change in process of time and a strength high enough to withstand stress generated in bonded portions by soldering due to a difference in thermal expansion coefficient between electronic components and a board, the work of dividing the board after soldering, warping of the board during the probing test, handling and the like.

A further object of the invention is to provide a connected structure and an electronic device with the use of an Sn-Ag-Bi based lead-free solder with low toxicity, which has an enough bonding strength while ensuring resistance to formation of whiskers, wettability of the solder and the like.

[0005]

[Means for Solving the Problem]

Accordingly, in order to achieve the objects of the invention, there is provided a lead-free solder-connected structure characterized in that an Sn-Ag-Bi based lead-free solder is connected to an electrode through an Sn-Bi based layer.

The present invention is characterized in that, in the lead-free solder-connected structure, the Sn-Bi based

layer contains 1 to 20 wt% Bi.

The present invention is characterized in that, in the lead-free solder-connected structure, there is provided a copper layer between the electrode and the Sn-Bi based layer.

The present invention is characterized in that the electrode is made of copper material.

The present invention is characterized in that an electrode in the lead-free solder-connected structure is a lead made of an Fe-Ni based alloy or a copper based alloy.

The present invention is characterized in that, in the lead-free solder-connected structure, the Sn-Ag-Bi based lead-free solder contains Sn as a primary component, 5 to 25 wt% Bi, 1.5 to 3 wt% Ag and up to 1 wt% Cu. [0006]

The present invention is an electronic device in which a first electrode formed on an electronic component and a second electrode formed on a circuit board are electrically connected to each other, and the electronic device is characterized in that an Sn-Bi based layer is formed on the first electrode, and the first electrode on which the Sn-Bi based layer is formed and the second electrode are connected to each other using an Sn-Ag-Bi based lead-free solder.

[0007]

The present invention is characterized in that, in

the electronic device, the Sn-Bi based layer contains 1 to 20 wt% Bi.

The present invention is characterized in that, in the electronic device, there is provided a copper layer between the first electrode and the Sn-Bi based layer.

The present invention is characterized in that the first electrode in the electronic device is a lead made of an Fe-Ni based alloy or a Cu based alloy.

The present invention is characterized in that the Sn-Ag-Bi based lead-free solder contains Sn as a primary component, 5 to 25 wt% Bi, 1.5 to 3 wt% Ag and up to 1 wt% Cu.

The present invention is a lead-free solder connected structure is characterized in that a lead-free solder connected to an electrode is of an Sn-Ag-Bi based solder containing Sn as a primary component, 5 to 25 wt% Bi, 1.5 to 3 wt% Ag and up to 1 wt% Cu.

As described above, with this configuration, it is possible to ensure a stable bonding interface having an enough bonding strength by applying the Sn-Ag-Bi based lead-free solder with low toxicity to an electrode of a lead frame or the like.

In addition, with the use of the Sn-Ag-Bi based lead-free solder with low toxicity, it is also possible to

ensure a bonding interface which is stable with respect to a change in process of time and which has a high enough strength to withstand stress generated in bonded portions by soldering due to a difference in thermal expansion coefficient between electric components and a board, the work of dividing the board after soldering, warping of the board during a probing test, handling and so on.

Furthermore, with the use of the Sn-Ag-Bi based lead-free solder with low toxicity, it is possible to ensure a bonding interface which has an enough strength and good resistance to occurrence of whiskers by forming sufficient fillets while keeping good wettability at soldering temperatures of, for example, 220 - 240°C.

[Mode for Carrying Out the Invention]

Hereinafter, a description of embodiments according to the invention will be provided.

One embodiment of the invention is an electronic device, comprising a first and a second electrodes both of which are bonded to each other with the use of a Pb-free solder with low toxicity, the first electrode being a QFP lead, a TSOP lead or the like in an electronic device such as a semiconductor device (e.g. LSI), for example, and the second electrode being on a circuit board. There is provided a structure in which, for example, the first electrode and the second electrode are bonded to each other

with the use of a Pb-free solder having low toxicity, as a Pb-free solder connection structure.

The Pb-free solder having low toxicity may be of an Sn-Aq-Bi based solder.

With the use of the Sn-Ag-Bi based Pb-free solder having low toxicity, it is required to obtain a bonding interface which is stable with respect to a change in process of time and has a bonding strength high enough to withstand stress generated in solder-bonded portions due to a difference in thermal expansion coefficient between an electronic component and a circuit board, the work of dividing the board after soldering, warping of the board during a probing test, handling or the like.

It is also required to obtain an enough bonding strength with the use of the Sn-Ag-Bi based Pb-free solder by forming a sufficient fillet shape while ensuring enough wettability at 220 - 240°C, which are suitable soldering temperatures with respect to heat resistance of the circuit boards and electronic components. If the solder has inferior wettability, a sufficient fillet shape can not be obtained resulting in that an enough bonding strength is not obtained or more active flux is required leading to an adverse influence on insulation resistance.

Furthermore, it is also necessary to ensure resistance to formation of whiskers or the like, because

short-circuit occurs between the electrodes if the whiskers are generated and grow on the electrode surface treated by plating or the like.

[0012]

As shown in Figs. 1 and 2, an Sn-Bi layer 2 is formed on the surface of an electrode 1 of a lead to obtain enough bonding strength as the electrode structure of the invention. Next, a selection of an electrode structure of the invention will be described. Such selection was made by evaluating mainly bonding strength, wettability and resistance to occurrence of whiskers based on the above requirements.

First, the results of an examination of the bonding strength obtained from between an Sn-Ag-Bi based solder and various kinds of electrode materials will be described. An outline of the experiment is illustrated in Fig. 3. Sample leads 4 were formed by plating Pb-free materials of Sn, Sn-Bi, Sn-Zn and Sn-Ag, which are considered to be usable as alternative materials for the conventional Sn-10Pb layer, onto leads each of which is an electrode made of an Fe-Ni based alloy (42 alloy). Besides, an evaluation was also performed for combinations with the conventional Sn-10Pb plating. The respective sample leads 4 were 3 mm wide by 38 mm long. It was bent to form right angles so that the length of the soldering section is 22 mm. The plating thickness was approximately 10 μ m for each composition.

The respective sample leads 4 were soldered to a Cu pad (Cu electrode) 7 on a glass epoxy substrate 6, which is a circuit board, with the use of a Pb-free solder 5 of a 82.2 wt% Sn-2.8 wt% Ag-15 wt% Bi (hereinafter referred to as Sn-2.8Ag-15Bi).

The Cu pad (Cu electrode) 7 on the glass epoxy substrate 6 had a size of 3.5 mm by 25 mm. The solder 5 was provided in the form of a foil of 0.1 mm by 25 mm by 3.5 mm. More specifically, the solder foil 5 was placed on the Cu pad 7 on the glass epoxy substrate 6 and the sample lead 4 being bent with the right angle was placed on the solder foil 5. Soldering was performed in the air at a maximum temperature of 220°C after preheating at 140°C for 60 seconds. A rosin flux containing chlorine was used when soldering. After soldering, cleaning was conducted with an organic solvent. Tensile tests were conducted in three cases: a sample lead immediately after soldering; another sample lead exposed to a high temperature of 125°C for 168 hours after soldering taking account of the deterioration of bonding strength due to a change with the passage of time; a further sample lead after soldering following the exposure thereof to 150°C for 168 hours to investigate the strength of the bonding interface in the case where wettability of lead is deteriorated. In the tensile test, the example lead was pulled vertically at a rate of 5mm/minute by gripping its distal end while the substrate is fixed. Then a maximum strength and a generally saturated constant strength were detected as a fillet strength and a flat portion strength, respectively, for the sample lead of each composition. The test was conducted ten times for each condition to determine an average value.

The test results of the fillet strength of the sample lead of each composition are shown in Fig. 4. plastic package devices such as ordinary QFP-LSIs, it is necessary that fillet strength be at least approximately 5 kqf in consideration of a difference in thermal expansion coefficient of printed-circuit boards. Due to this fact, it became apparent that an adequate bonding interface cannot be obtained in the case of Sn-Zn, Sn-Ag and Sn-Pb layers although the fillet portion strength equal to 5 kgf or more could be obtained in the case of sample leads in which Sn-Bi based layers other than an Sn-Bi based layer containing Sn and 23 wt% Bi are plated on the Fe-Ni based alloy (42 alloy). In addition to these sample leads, further three types of sample leads were prepared by providing an Ni plating layer having a thickness of about 2 μm onto the 42 alloy and plating the Ni layer with Au layer, a Pd layer, and a Pd layer with a further Au layer, respectively. Soldering was performed in the same manner and the bonding interface strength was examined; however, enough fillet strength was incapable of being obtained as

shown in Fig. 4. Accordingly, it became apparent that it is necessary to apply an Sn-Bi layer to a lead of an electrode.

[0014]

Wettability to the Sn-2.8Ag-15Bi solder was tested by the meniscograph method in the Sn-Bi alloy plated leads which showed enough bonding strength in the above tensile test conducted on sample leads of various compositions. A flux of less activity was used in order to investigate wettability. Test pieces were obtained by cutting the above sample leads into a length of 1 cm. The wettability test was conducted under the test conditions: a solder bath temperature of 220°C, an immersion speed of 1 mm/minute, an immersion depth of 2 mm and an immersion time of 20 seconds. The time which elapses till the load recovers to 0 (zero) was regarded as wetting time and the load after immersion for 20 seconds was regarded as wetting force. Wettability was determined in two cases: a lead immediately after plating and a lead exposed to $150\,^{\circ}\mathrm{C}$ for 168 hours after plating. Measurements were made ten times for each test condition to obtain an average value.

[0015]

The wetting time and wetting force for each composition are shown in Fig. 5 and Fig. 6, respectively. It became apparent from the result of wetting time shown in Fig. 5 that the higher the Bi content, the better

wettability in the Sn-Bi based plated leads tested immediately after plating, while wettability is deteriorated at below 1 wt% Bi and at 23 wt% Bi when the leads are exposed to a high temperature of 150°C for 168 hours. It can be said that at Bi contents of below 1 wt%, wettability was low because the wetting time became long while the wetting force was ensured as shown in Fig. 6. Therefore, it became apparent that a desirable Bi content is from 1 to 20 wt% in order to obtain sufficient wettability even with the Sn-Bi based layer.

Stress generated in the interface is high when materials with a great difference in thermal expansion coefficient are bonded together, when materials are used in an environment of great temperature difference, and the like. The bonding strength in the interface must be approximately 10 kgf or more in order to ensure sufficient reliability. Therefore, it became evident from Fig. 4 that fillet strength of 10 kgf or more cannot be obtained by directly providing an Sn-Bi based layer onto the Fe-Ni based alloy (42 alloy). It is believed that this is because the compounds at the interface are not sufficiently formed. Therefore, a Cu plating layer of about 7 µm on average was applied to the Fe-Ni based alloy (42 alloy) and an Sn-Bi based plating layer was applied to this cu layer in order to raise the reactivity with the solder in the

interface and bonding strength was measured. The fillet strength, including the case of no Cu layer, is also shown in Fig. 7. Bonding strength of not less than 10 kgf was obtained with the exception of the case of 23 wt% Bi and the effect of the under-layer of Cu was capable of being verified. By adopting this electrode structure it was possible to obtain a bonding strength of about 12.1 kgf or more that is obtained immediately after soldering of a lead made of the 42 alloy on which an Sn-10Pb layer is formed, which is soldered by means of a eutectic Sn-Pb solder, and whose bonding strength is also shown as a comparative solder in Fig. 7. Furthermore, as shown in Fig. 8, flat portion strength was also capable of being improved by forming a Cu layer under the Sn-Bi layer. The Cu layer may be applied to the 42 alloy as described above when a lead frame of 42 alloy is used. However, when a Cu lead frame is used, this lead frame may be allowed to serve as the Cu layer or a further Cu layer may be formed in order to eliminate the effect of other elements which may sometimes be added to the lead frame material to improve rigidity. The wettability of the sample leads to which this Cu layer is applied is also shown in Figs. 5 and 6. There is scarcely any effect of the Cu layer and sufficient wettability was capable of being obtained at 1 - 20 wt% Bi, although wettability also deteriorated at Bi contents of not more than 1 wt% when the lead frames were exposed to a

high temperature. Incidentally, an Sn-2.8Ag-15Bi was used in the samples shown in Figs. 7 and 8. However, the formation of an under-layer of Cu is effective in improving bonding strength even in groups of low Bi content, for example, an Sn-2Ag-7.5Bi-0.5Cu alloy.

The method of application of the above Sn-Bi based layers and Cu layers is not limited to plating and these layers can also be formed by dipping, deposition by evaporation, roller coating or metal powder application.

Thus, in order to investigate the reason why various types of the electrode materials have different strengths from one another, cross-sectional surfaces of bonding portions were observed after polishing. Further the fractured surfaces of samples subjected to the tensile test were observed under an SEM. The results obtained in the typical combinations are described below.

First, Fig. 9 shows an observation result in the case where a lead obtained by applying an Sn-10Pb plating directly onto the conventional Fe-Ni based alloy (42 alloy) is bonded using an Sn-Ag-Bi based solder. In this combination, Pb-Bi compounds agglomerated at the interface and fracture occurred in the interface between the 42 alloy and the solder. A small amount of Sn was detected on the fractured 42 alloy surface of the lead and it is believed that the Sn in the solder formed compounds with the 42

alloy of lead. It is believed, therefore, that agglomeration of the above compounds of Pb and Bi at the interface reduced the contact area between Sn and 42 alloy, greatly weakening bonding strength.

[0018]

Next, Fig. 10 shows an observation result in the case where the Sn-10Pb plating was replaced with an Sn-4Bi plating. The compound layer formed in the interface was thin and fracture occurred similarly at the interface between 42 alloy and solder. However, Bi remained granular crystals, which do not cause a decrease in the area of bond between Sn and 42 alloy so much as in the case of an Sn-10Pb. It is believed that this is the reason why bonding strength of not less than 5 kgf was capable of being obtained. Auger analysis revealed that the then compound layer is an Sn-Fe layer of about 70 nm.

Fig. 11 shows an observation result in the case where a Cu layer was formed on under the Sn-4Bi layer. It was found that a thick layer of compounds of Cu and Sn is formed in the interface. Fracture occurred in the interface between this compound layer and the solder or in the compound layer. The fractured surface was almost flat in the case shown in Fig. 10 where the Sn-Bi layer was directly formed on the 42 alloy lead, whereas it was uneven in the case where the Cu layer was present. For this reason, it is believed that this difference in the

fractured surface resulted in the improvement in bonding strength. Incidentally, similar investigation results were obtained also from other Sn-Ag-Bi based solder compositions.
[0019]

Occurrence of whiskers was investigated for the above sample leads of each composition. The formation of whiskers was observed on the surfaces of the sample leads to which an Sn-Zn plating layer was applied. It has been hitherto said that Sn plating presents a problem in resistance to the formation of whiskers. However, the occurrence of whiskers was not observed in the Sn-Bi based layers and there was no problem in resistance to formation of whiskers.

Accordingly, with the use of the electrode structures of the invention, the bonding portions excellent in bonding strength, wettability and resistance to occurrence of whiskers can be obtained with the use of Sn-Ag-Bi based solders.

[0020]

The reason why Sn-Ag-Bi solders containing Sn as a primary component, 5 to 25 wt% Bi, 1.5 to 3 wt% Ag and optionally 0 to 1 wt% Cu were selected is that solders of the composition in these ranges permit soldering at 220 - 240°C and that these solders have almost the same wettability as eutectic Sn-Ag solders, which have hitherto been field proven for Cu, and provide sufficient

reliability at high temperatures. More specifically, Sn-Ag-Bi based solders have a composition (a ternary eutectic alloy) which melts at approximately 138°C when the Bi content is not less than approximately 10 wt% and it is concerned about that these portions might have an adverse influence on reliability at high temperature. However, the precipitation of a ternary eutectic composition is controlled to levels that pose no problem in practical use and high-temperature strength at 125°C is also ensured. Accordingly, practical and highly reliable electronic articles can be obtained by soldering the above electrode using the solder of this composition.

[0021]

[Example 1]

The cross-sectional structure of a lead for QFP-LSI is shown in Fig. 1. This illustrates a part of the cross-sectional structure of the lead. An Sn-Bi based layer 2 was formed on a lead 1 that is of an Fe-Ni based alloy (42 alloy). The Sn-Bi based layer 2 was formed by plating and its thickness was about 10 μm . The Bi content of Sn-Bi plating layer was 8 wt%. The above QFP-LSI having this electrode structure was soldered to a glass epoxy substrate, which is a circuit board, with utilization of an Sn-2.8Ag-15Bi-0.5Cu solder. The soldering was carried out in a reflow furnace of a nitrogen environment at a peak temperature of 220°C. Thus, it was possible to obtain

bonding portions having sufficient bonding strength. Similarly, a reflow soldering was carried out on a glass epoxy substrate in the air at 240°C with the use of an Sn-2Ag-7.5Bi-0.5Cu solder. Bonded portions produced by reflow heating have high reliability especially at a high temperature.

[0022]

[Example 2]

The cross-sectional structure Of a TSOP lead is shown in Fig. 2 that is a part of the lead structure. A Cu layer 3 is formed on a lead 1 which is of an Fe-Ni based alloy (42 alloy) and an Sn-Bi based layer 2 is formed on this Cu layer. The Cu layer 3 and Sn-Bi based layer 2 were formed by plating. The thickness of the Cu layer 3 was about 8 μ m and that of the Sn-Bi based plating layer was about 10 μm . The Bi content of the Sn-Bi plating layer was 5 wt%. Because of high rigidity of the TSOP lead, when it is used at a high temperature or under a condition that heat generation occurs in the device itself, stress generated at the interface is greater as compared with the QFP-LSI. In such cases, it is necessary to form an interface with sufficient bonding strength high enough to withstand this interface stress and the Cu layer under the Sn-Bi layer is effective for this purpose. [0023]

The TSOP was soldered to a printed-circuit board in

a vapor reflow furnace with the use of an Sn-Ag-Bi based solder and the thermal cycle test was conducted. The test was conducted under the two test conditions: one hour per cycle of -55°C for 30 minutes and 125°C for 30 minutes; and one hour per cycle of 0°C for 30 minutes and 90°C for 30 minutes. After 500 cycles and 1,000 cycles the cross section was observed and the condition of formation of cracks was investigated. The cycle test result of crack occurrence was compared with a case where a TSOP of the same size having 42 alloy leads on which an Sn-10Pb alloy layer is directly formed, was soldered using a eutectic Sn-Pb solder. Although cracks were formed early in the thermal cycles of -55°C/125°C, no problems arose with the thermal cycles of 0°C/90°C and a bonding interface which is adequate for practical use was obtained.

[0024]

[Example 3]

The electrode structures according to this invention can also be applied to an electrode on a board. For example, solder coating is effective in improving the solderability of boards. Conventionally, there have been used lead-containing solders such as an Sn-Pb solder or a eutectic Sn-Pb solder. Thus, the Sn-Bi layer according to the invention can be used to make the solder for coating lead-free. Furthermore, because the electrode of a board is made of copper, sufficient bonding strength can be

obtained when an Sn-Ag-Bi based solder is used. An example in which this structure is applied is shown; an Sn-8Bi layer of about 5 µm was formed by roller coating on a Cu pad (Cu electrode) on a glass epoxy substrate, which is a circuit board. Wettability to boards and bonding strength were improved, because the solder layer was formed.

[Effects of the Invention]

According to the present invention, an electrode structure can be realized, which is suitable for an Sn-Ag-Bi based solder excellent as a lead-free material.

According to the present invention, a bonded structure by a lead-free solder can be realized with the use of a lead-free Sn-Ag-Bi based solder with low toxicity for an electrode such as a lead frame and the like, in which an bonding interface which is stable and has sufficient bonding strength can be obtained.

According to the present invention, an electronic article can be realized with the use of a lead-free Sn-Ag-Bi based solder with low toxicity, which has a bonded structure by the lead-free solder, which can provide a stable bonding interface with respect to a change in process of time and a strength high enough to withstand stress generated in bonded portions by soldering due to a difference in thermal expansion coefficient between electric devices and a board, the work of dividing the

board after soldering, warping of the board during a probing test, handling and the like.
[0026]

According to the present invention, with the use of a lead-free Sn-Ag-Bi based solder with low toxicity, it is possible to obtain sufficient bonding strength by forming adequate fillets while ensuring sufficient wettability, for example, at 220 - 240° and to ensure resistance to formation of whiskers, etc.

According to soldering electronic devices with utilization of an Sn-Ag-Bi solder makes it possible to obtain an interface which has sufficient bonding strength and to ensure wettability which is sufficient for practical use. There is no problem in resistance to formation of whiskers. Thus it is possible to realize lead-free electrical appliances that are environmentally friendly by using the same equipment and process as those used conventionally.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 is a cross-sectional view of a lead for a QFP-LSI according to the invention.

[Fig. 2]

Fig. 2 is a cross-sectional view of a lead for a TSOP according to the invention.

[Fig. 3]

Fig. 3 is a schematic diagram showing a testing method of evaluating solder-bonding strength.

[Fig. 4]

Fig. 4 is a diagram showing evaluation results of fillet strength with regard to various types of metallized leads according to the invention.

[Fig. 5]

Fig. 5 is a diagram showing evaluation results of wetting time with regard to various types of metallized leads according to the invention.

[Fig. 6]

Fig. 6 is a diagram showing evaluation results of wetting force with regard to various types of metallized leads according to the invention.

[Fig. 7]

Fig. 7 is a diagram showing evaluation results of fillet strength in the case where there is formed a copper layer according to the invention.

[Fig. 8]

Fig. 8 is a diagram showing evaluation results of flat portion strength in the case where there is formed a copper layer according to the invention.

[Fig. 9]

Fig. 9 shows an observation result of an interface region of a solder and a lead of an Fe-Ni alloy (i.e. 42 alloy) on which an Sn-10Pb alloy plating is provided

according to the prior art, wherein (a) is a cross-sectional view of the interface region, and (b) are fractured surfaces on the lead side and the solder side, respectively.

[Fig. 10]

Fig. 10 shows an observation result of an interface region of a solder and a lead of an Fe-Ni alloy (i.e. 42 alloy) on which an Sn-4Bi alloy plating is provided according to the invention, wherein (a) is a cross-sectional view of the interface region, and (b) are fractured surfaces on the lead side and the solder side, respectively.

[Fig. 11]

Fig. 11 shows an observation result of an interface region of a solder and a lead of an Fe-Ni alloy (i.e. 42 alloy) of the invention on which an under copper layer and an upper Sn-4Bi alloy plating is provided according to the invention, wherein (a) is a cross-sectional view of the interface region, and (b) are fractured surfaces on the lead side and the solder side, respectively.

[Explanation of Reference Numerals]

1: Fe-Ni alloy lead (electrode), 2: Sn-Bi based layer, 3: Cu layer, 4: sample lead, 5: solder, 6: glass epoxy board, 7: Cu pad (Cu electrode)

[Name of Document] Abstract of the Disclosure
[Abstract]

[Object] To provide a Pb-free solder connected structure and an electronic device capable of obtaining an interface that has a sufficient bonding strength and stability with respect to a change in process of time, and that ensures sufficient wettability and resistance to formation of whiskers, etc.

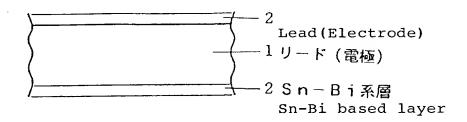
[Solving Means] The present invention is characterized by applying a lead-free Sn-Ag-Bi alloy solder, which is predominant as a Pb-free solder, to an electrode to which an Sn-Bi based layer is applied thereon. The Sn-Bi layer, preferably, contains 1 to 20 wt% Bi in order to obtain good wettability of the solder. In order to obtain desirable bonding characteristics having higher reliability in the invention, a copper layer is provided under the Sn-Bi layer, thereby obtaining a sufficient bonding strength.

[Selected Drawing] Fig. 1

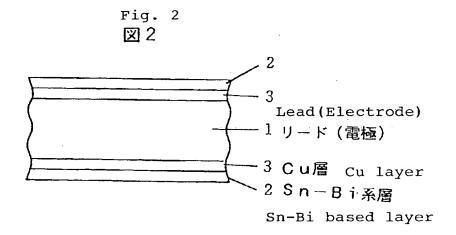
【書類名】 図面 (Name of Document) Drawing

【図1】

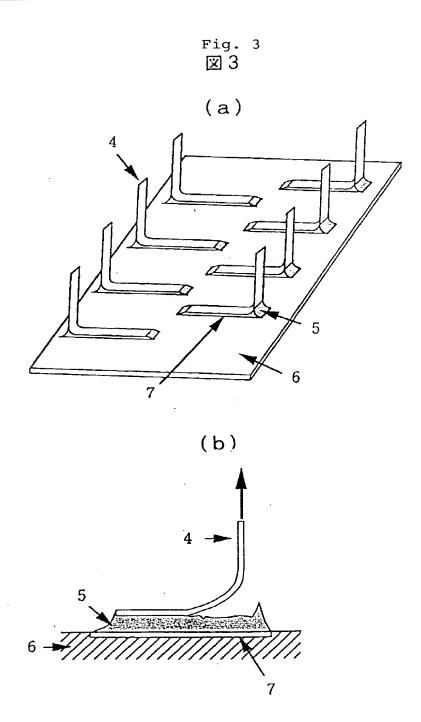
Fig. 1 図1



[図2]

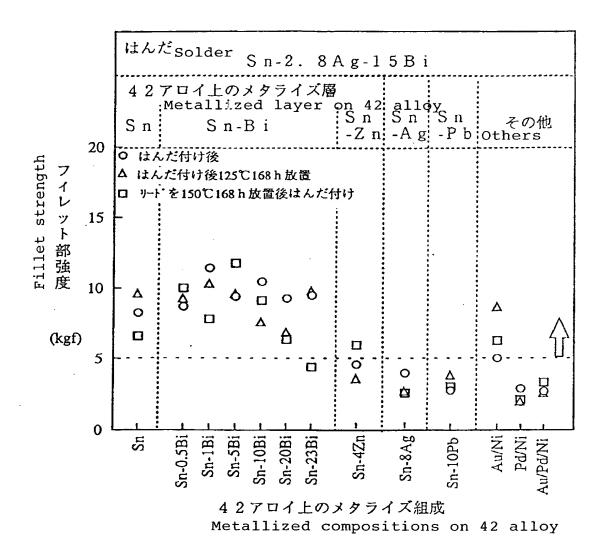


[図3]



【図4】

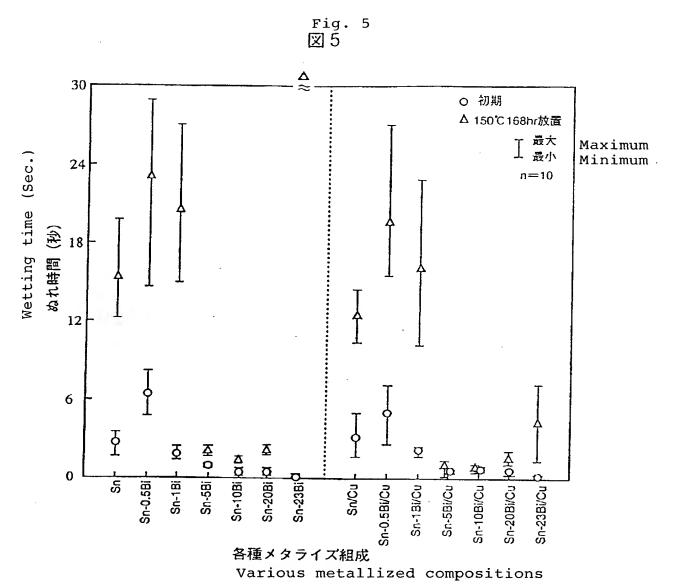
Fig. 4 図4



o after soldering

A exposed to 125° C for 168 hrs after soldering

【図5】

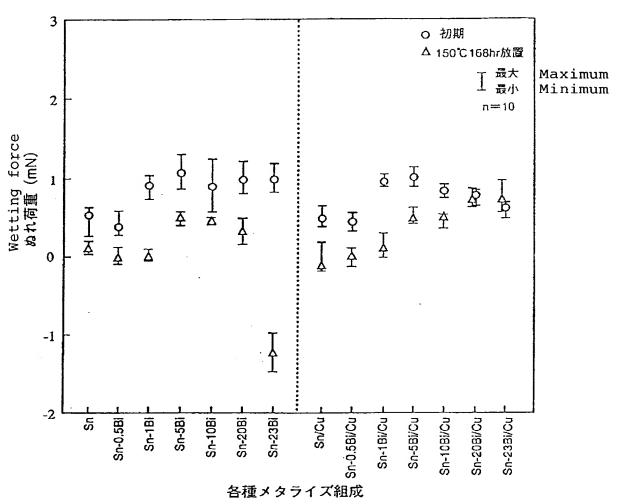


O soon after plating

 \triangle exposed to 150°C for 168 hrs

【図6】

Fig. 6 図6

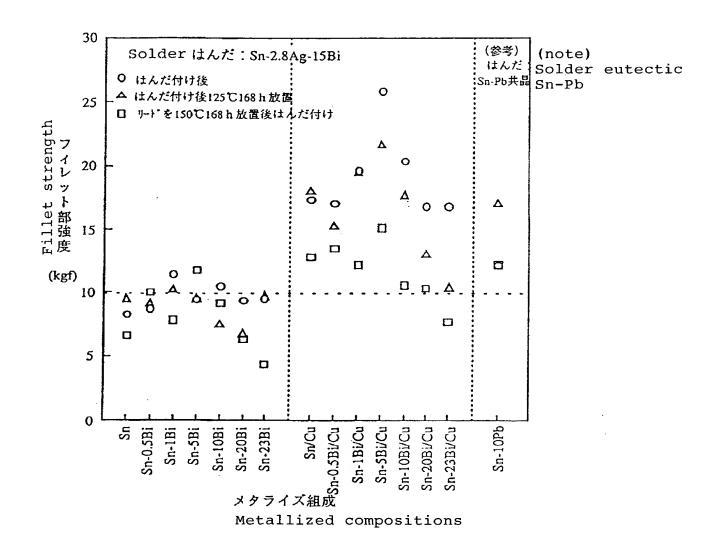


Various metallized compositions

- O soon after plating
- \triangle exposed to 150 $^{\circ}$ C for 168 hrs

【図7】

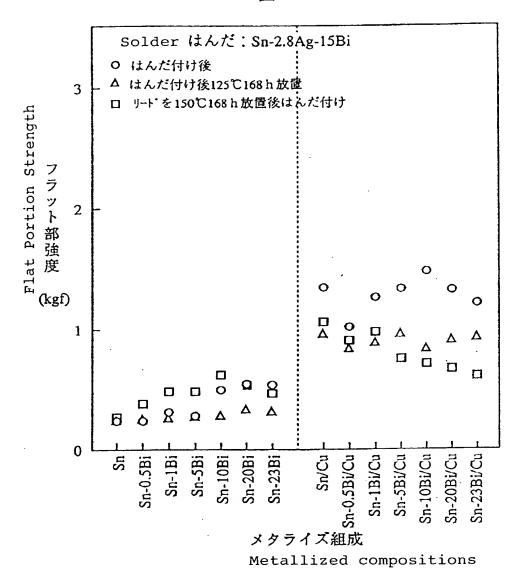
Fig. 7 図7



- O after soldering
- riangle exposed to125 $^{\circ}$ C for 168 hrs after soldering

【図8】

Fig. 8 図8

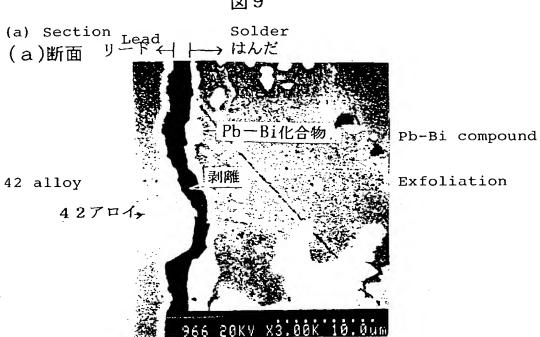


O after soldering

 Δ exposed to 125 $^{\circ}$ C for 168 hrs

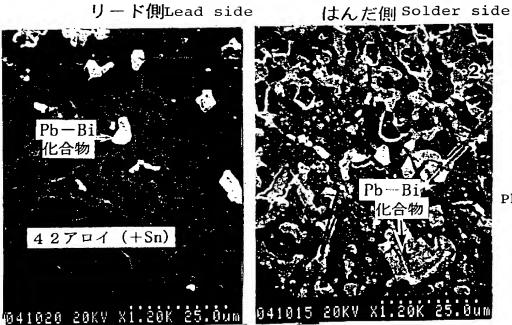
[図9]





(b)剥離部(b) Fractured portion





Pb-Bi compound

Pb-Bi compound

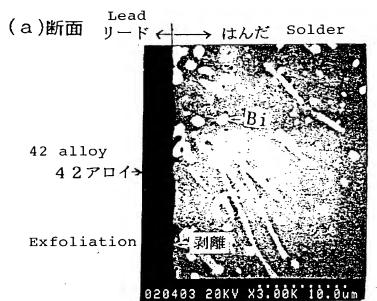
42 alloy

【図10】

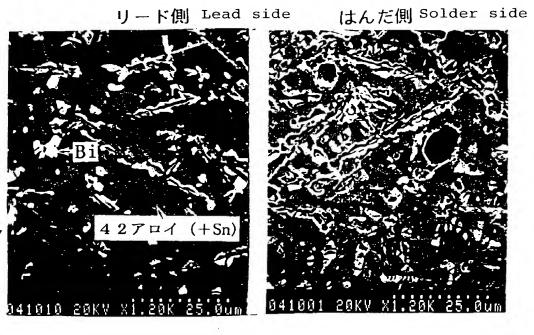
Fig. 10

図10

(a) Section



- (b) Fractured portion
- (b)剥離部



42 alloy

【図11】

Fig. 11 図11

-Sn化合物

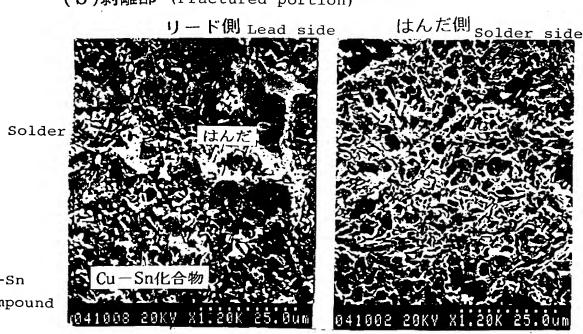
(a) Section

(a)断面 Lead リード Cu-Sn compound Cu一Sn化合物 →はんだ Solder 42 alloy 42アロイナ

Cu-Sn compound

Exfoliation

(b)剥離部 (Fractured portion)



020422 20KV X3.00K 10.0um

Cu-Sn compound